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# Overview

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## Introduction

Solid phase microextraction (SPME) has been applied to a diverse range of analytes and sample types. The growth in the application of SPME, since its inception in 1990, can be seen in **Figure 1** (information from the *Science Citation Index*, February 1999). SPME is used as both a method of preconcentration and as a sampling device for (predominantly) chromatographic analysis. SPME has been used in conjunction with a range of other techniques, such as, ultraviolet and infrared spectroscopy, Raman spectroscopy and mass spectrometry, but it is its use in chromatographic analysis which is the focus of this article. SPME has most commonly been coupled to gas chromatography (GC), although some applications have coupled it to high-performance liquid chromatography (HPLC) (**Figure 2**). The following discussion will concentrate primarily on the use of SPME coupled with GC.

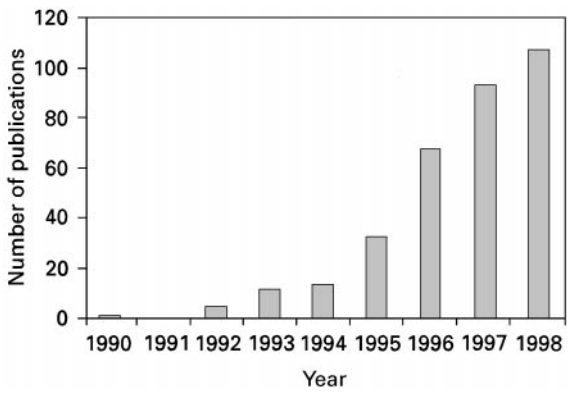


**Figure 1** Frequency of SPME publications per year (information from the *Science Citation Index,* February 1999, Copyright International Scientific Communications, Inc.).

The SPME device consists of a fused silica fibre, coated with a stationary phase (**Table 1**) and mounted in a syringe-type holder (**Figure 3**). The SPME holder has two functions: to provide protection for the fibre and allow insertion into the hot environment of the GC injector using a needle. As samples and standards are normally introduced into a GC via a syringe the use of this device offers no additional complexity.

At rest the fused silica-coated fibre is retracted within the protective needle of the SPME holder. In operation however, the fibre is exposed to the analyte within its matrix (air, water, solid) for a predetermined amount of time. The active length of the fibre is typically 1 cm. Two common approaches for sample extraction are employed; direct and headspace (**Figure 4**). The first involves direct contact between the coated fibre and the sample matrix; in this way analytes within the sample are able to be transported to the fibre coating. This transportation can be achieved by several means. In the case of liquid (or solid samples that have been mixed with an aqueous solution, i.e. a slurry), transportation is achieved by agitation of the sample vial, agitation of the fibre, stirring or sonication of the sample solution. For gaseous samples, natural convection is usually sufficient. In the headspace mode, the process relies on the release of volatile compounds from the sample matrix. This may be achieved by heat, chemical modification or the inherent volatility of the analyte.

After sampling, the fibre is retracted within its holder for protection until inserted in the hot injector

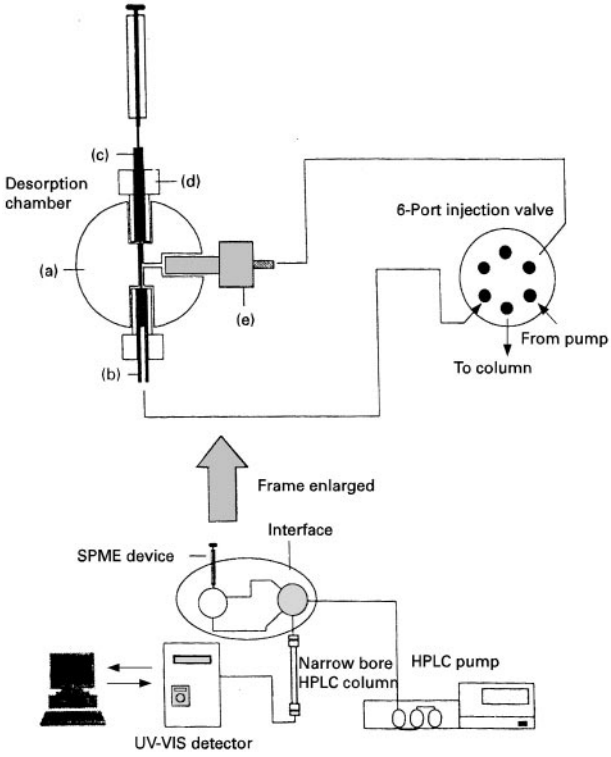


**Figure 2** Solid phase microextraction–high-performance liquid chromatography interface (reproduced with permission, from *Analytical Chemistry* 67: 2530, 1995, Copyright American Chemical Society).

of the GC or mobile phase of the HPLC; desorption of analytes occurs due to the influence of temperature (GC) or organic solvent (HPLC). In either case the fibre is exposed for a particular time to allow for effective desorption of the analytes. As the coating on the fibre is selective towards the analyte, it is common to find that no solvent peaks are present in the subsequent chromatograms. As the fibre coating is selective towards the target analytes it is important to select the most appropriate fibre coating for the sampling process. **Figure 5** compares the influence of three fibre coatings, i.e. polystyrene–divinylbenzene (XAD), polyacrylate, and polydimethylsiloxane (PDMS) for the extraction of 49 organophosphorus pesticides from a water sample. The selectivity of each fibre coating is evident from the chromatograms (Figure 5).

It is important to note that the fibre can equally adsorb analytes from the atmosphere as well as the sample (in some cases the atmosphere may be the sample). Extreme caution should be taken first of all to clean the fibre. This can be done, for example, by exposing the fibre to the hot injector of the GC before sampling. Also, it is important to minimize the time between the sorption step and the subsequent desorption and analysis step.

**Table 1** Commercially available fibre coatings

- 7 μm Polydimethylsiloxane (bonded)
- 30 μm Polydimethylsiloxane (non-bonded)
- 100 μm Polydimethylsiloxane (non-bonded)
- 85 μm Polyacrylate (partially crosslinked)
- 60 μm Polydimethylsiloxane/divinylbenzene (partially crosslinked)
- 65 μm Polydimethylsiloxane/divinylbenzene (partially crosslinked)
- 75 μm Polydimethylsiloxane/Carboxen (partially crosslinked)
- 65 μm Carbowax/divinylbenzene (partially crosslinked)
- 50 μm Carbowax/Template resin (partially crosslinked)

Quantitation in SPME is achievable in much the same way as for any other sample analysis. For example, in GC a series of standard solutions are prepared in organic solvent over the appropriate concentration range for the analytes under investigation. From the results obtained a calibration graph can be constructed [a plot of signal intensity (area or peak height) versus concentration]. Then, an organic solvent extract of the unknown is injected into the GC and its response compared to the calibration graph. In the same manner for SPME, a series of standard solutions need to be prepared in aqueous solution or soil slurry form. The fibre is then exposed to the solution (or soil slurry) for a prespecified time and then introduced into the hot injector of the GC. In

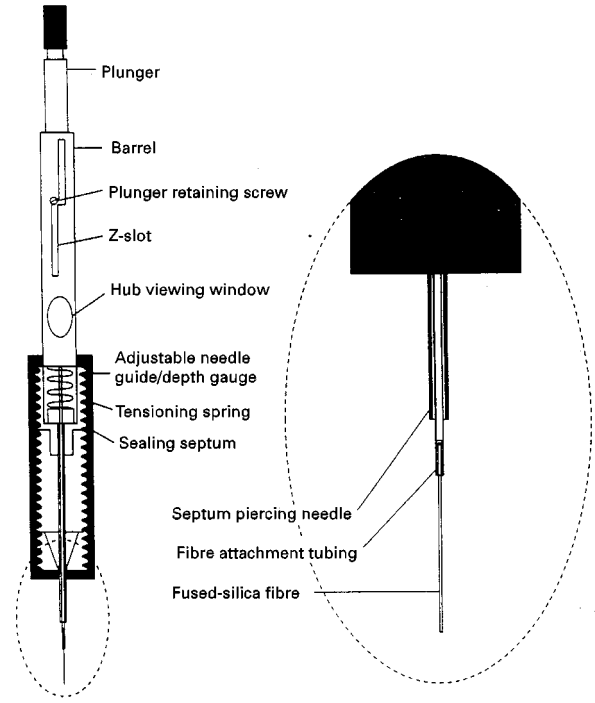


**Figure 3** Solid phase microextraction device (reproduced with permission from *Analytical Chemistry* 66: 844A, 1994, Copyright American Chemical Society).

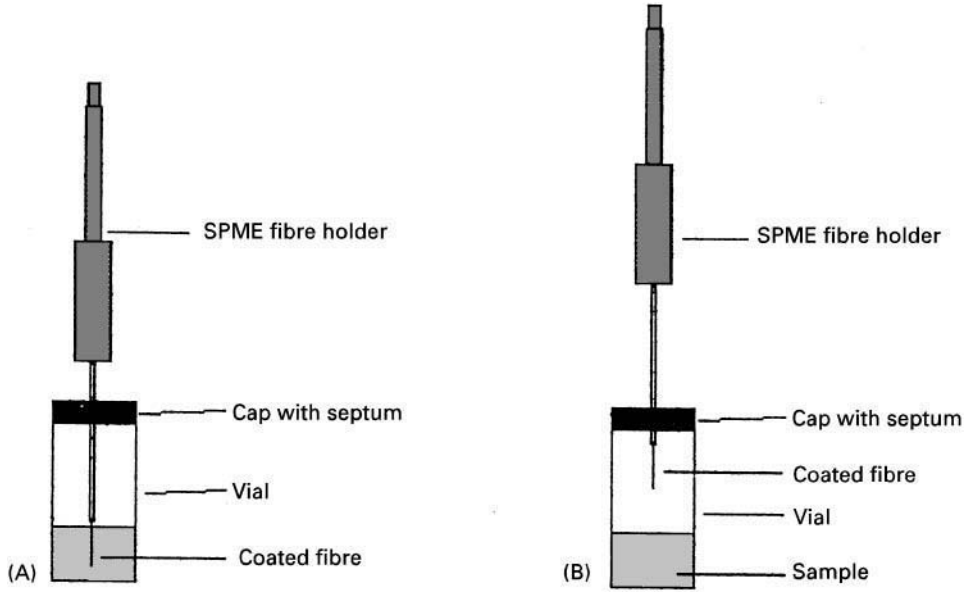


**Figure 4** Common approaches for SPME. (A) Direct SPME and (B) headspace SPME.

this manner a calibration graph can be constructed. Similarly, an aqueous SPME extract (or slurry extract) of an unknown sample is injected in the GC and its signal response compared with the calibration graph. Calibration is also done in this manner for headspace SPME, the difference being that the fibre is exposed to the headspace above the sample only and not placed in the solution or soil slurry itself. It is common practice to utilize an internal standard for all quantitative analysis. Calibration is also possible using the method of standard additions. For further information on quantitative headspace methods see the book by Kolb and Ettre listed in the Further Reading section.

The diversity of applications of SPME is continually expanding, limited only by people's ingenuity, so it is not unfamiliar to find applications of SPME in such diverse areas as environmental and clinical, food and pharmaceutical, forensic and military use. However, the most popular application area is environmental analysis (water and soil). In order to provide examples of the diversity of applications, selected areas have been considered. For further information, the reader is recommended to consult the Further Reading Section or the current scientific literature.

## Extraction of Analytes from Aqueous Matrices

Analysis of polar and labile analytes in aqueous matrices usually involves extraction and preconcentration. This has traditionally been based on liquid–liquid extraction (LLE). In this context, a small volume of organic solvent is added to a larger volume of the aqueous sample and shaken (it may be necessary to 'salt-out' the analytes, this is done by saturating the aqueous sample with an inorganic salt). The organic phase containing the analytes is then analysed. [Note: additional preconcentration may be required using evaporation in a stream of inert gas (manual or automated) or vacuum evaporation.] However, if the analytes are sufficiently volatile they can be purged from an aqueous sample using a gas, such as nitrogen, preconcentrated by trapping on a suitable sorbent, e.g. Tenax, at low temperature and eluted by rapidly heating the trap. The analytes are then directly transferred into a gas chromatograph for separation and detection. This procedure, known as dynamic headspace or 'purge and trap' sampling is an effective procedure for volatile analytes. An alternative to the requirements for extraction and preconcentration of non-volatiles is solid phase extraction (SPE).

SPE uses a stationary phase, such as $C_{18}$-silica, to adsorb analytes from a large volume of sample solution. Elution of analytes is then achieved by using a small volume of organic solvent. In this manner, effective extraction and preconcentration is achieved. The use of SPME takes this method a stage further in miniaturization.

Effective extraction and preconcentration of analytes in aqueous matrices can be achieved using SPME. Two approaches are commonly used. In the first approach, the fibre is inserted directly into an aqueous sample for a prespecified time, with or

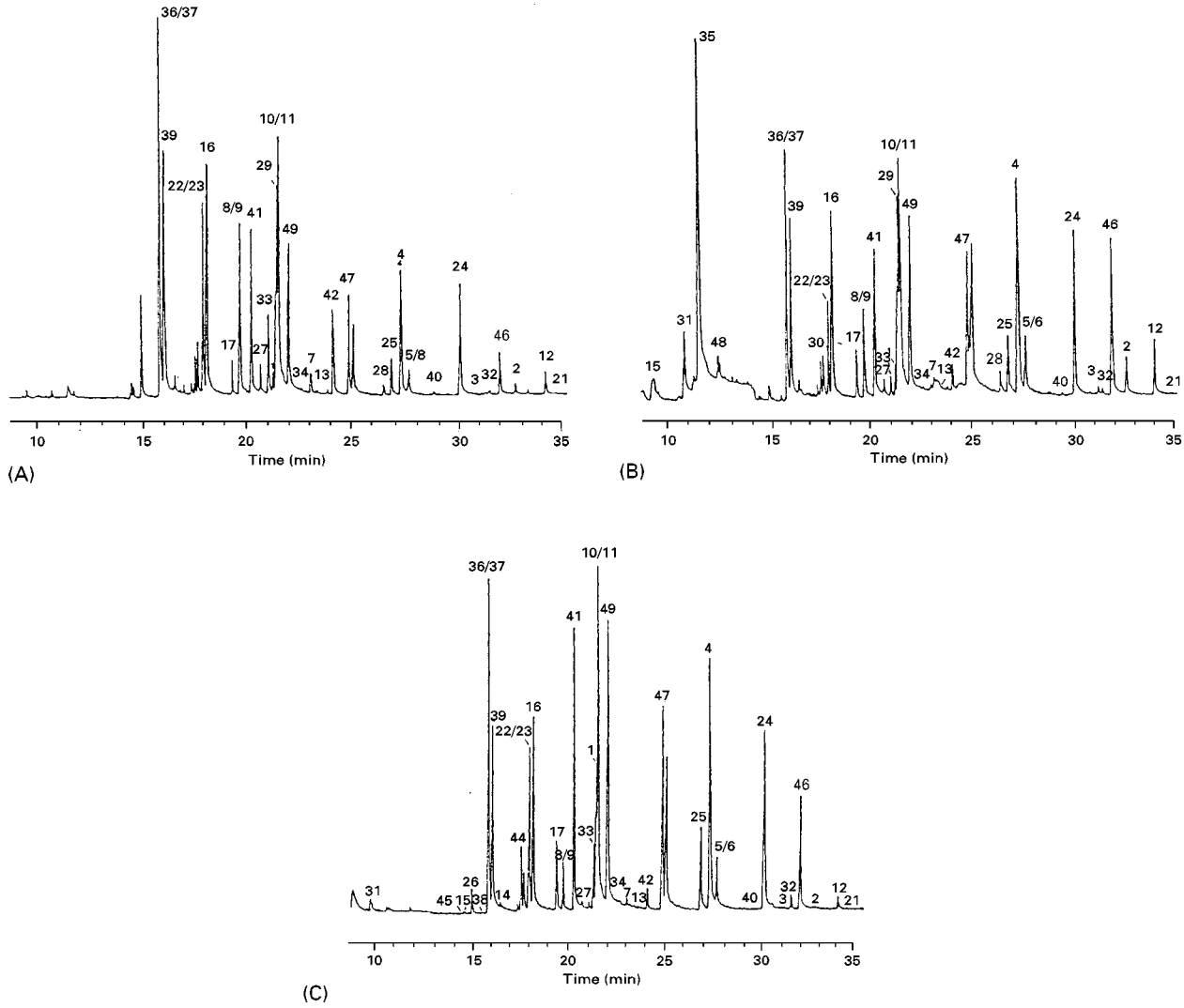


**Figure 5** SPME of 3 μg $L^{-1}$ organophosphorus pesticides. (A) 15 μm XAD polystyrene–divinylbenzene)-coated fibre, (B) 85 μm polyacrylate-coated fibre, and (C) 30 μm polydimethylsiloxane-coated fibre. (Reproduced with permission from *Journal of High Resolution Chromatography* 20: 487, 1997, Copyright John Wiley & Sons Limited.) GC conditions: column 30 m length × 0.25 mm internal diameter × 0.25 μm film PTE-5 fused silica open tubular; temperature programme 60°C (4 min hold) to 150°C at 30°C $min^{-1}$ and from 150 to 300°C at 5°C $min^{-1}$ (hold for 3 min). SPME conditions: 15 μm XAD coated fibre; absorption time, 30 min; desorption time, 20 min at 270°C. Eighty-five μm polyacrylate coated fibre; adsorption time, 30 min; desorption time, 20 min at 280°C. Thirty μm polydimethylsiloxane coated fibre; adsorption time, 30 min; desorption time, 20 min at 300°C. Spiking level was 3 μg $L^{-1}$ per compound; sample volume was 1.5 mL. *Peak identification*: 1 = aspon; 2 = azinphos-ethyl; 3 = azinphos-methyl; 4 = bolstar; 5/6 = carbophenothion/famphur; 7 = chlorfenvinphos; 8/9 = chlorpyrifos-methyl/parathion-methyl; 10/11 = chlorpyrifos/parathion-ethyl; 12 = coumaphos; 13 = crotoxyphos; 14 = demeton-O; 15 = demeton-S; 16 = diazinon; 17 = dichlorfenthion; 18 = dichlorvos; 19 = dicrotophos; 20 = dimethoate; 21 = dioxathion; 22/23 = disulfoton/phosphamidon; 24 = *O*-ethyl-*O*-(4-nitrophenyl)phenylphosphono-thioate (EPN); 25 = ethion; 26 = ethoprop; 27 = fenitrothion; 28 = fensulfothion; 29 = fenthion; 30 = fonophos; 31 = hexamethylphosporamide (HMPA); 32 = leptophos; 33 = malathion; 34 = merphos; 35 = mevinphos; 36/37 = monocrotophos/sulfotepp; 38 = naled; 39 = phorate; 40 = phosmet; 41 = ronnel; 42 = stirophos; 43 = tetraethylpyrophosphate (TEPP); 44 = terbufos; 45 = thionazin; 46 = tri-*O*-cresylphosphate; 47 = tokuthion; 48 = trichlorfon; and 49 = trichloronate.

without stirring and with or without the addition of salt. The fibre is then retracted into its protective holder and the adsorbed analytes desorbed in either the hot injector of the GC or in the mobile phase of an HPLC system. This approach is to be favoured for the more non-volatile, labile type of analytes. The alternative approach is to place a small volume of the liquid sample in a sealed vial and to insert the fibre into the headspace above the sample for a prespecified time. Again, stirring may be beneficial as well as the addition of salt. In addition, warming the sample vial may prove to be beneficial by increasing the concentration of volatile analytes in the headspace above the sample.

**Table 2** Limits of detection (ng $L^{-1}$) for selected pesticides from water using a 95 μm polyacrylate coated fibre

| *Compound* | *FID*[a] | *NPD*[b] | *MS*[c] | *MS*[d] |
|---|---|---|---|---|
| EPTC | 2000 | 50 | 0.8 | 16 |
| Butylate | 1000 | 20 | 0.1 | 1 |
| Vernolate | 1000 | 20 | 0.5 | 2 |
| Pebulate | 1000 | 20 | 1 | 19 |
| Molinate | 2000 | 60 | 0.3 | 12 |
| Propachlor | 6000 | 800 | 15 | 16 |
| Cycloate | 800 | 20 | 0.05 | 1 |
| Trifluralin | 400 | 30 | 0.02 | 1 |
| Benfluralin | 300 | 30 | 0.4 | 1 |
| Simazine | 1000 | 70 | 1 | 15 |
| Atrazine | 7000 | 40 | 3 | 11 |
| Propazine | 10 000 | 50 | 0.3 | 6 |
| Profluralin | 200 | 30 | 0.1 | 1 |
| Terbacil | 15 000 | 200 | 1 | 9 |
| Metribuzin | 14 000 | 200 | 3 | 19 |
| Bromacil | 19 000 | 400 | 0.1 | 8 |
| Metolachlor | 1000 | 200 | 0.01 | 8 |
| Isopropalin | 300 | 10 | 0.1 | 1 |
| Pendimethalin | 200 | 20 | 0.1 | 1 |
| Oxadiazon | 300 | 30 | 0.01 | 1 |
| Oxyfluorofen | 200 | 300 | 6 | 1 |
| Hexazinone | 2000 | 6000 | 1 | 15 |

[a] Determined from 100 μg $L^{-1}$ solutions.
[b] Determined from 10 μg $L^{-1}$ solutions.
[c] Determined from 0.01 μg $L^{-1}$ solutions.
[d] Calculated for the line of best fit with a zero intercept, over the range 0.1–100 μg $L^{-1}$($n = 3$). Values (a)–(c) are from Boyd-Boland AA and Pawliszyn J (1995) *Journal of Chromatography* 704: 163. Values for (d) are from Boyd-Boland AA *et al.* (1996) *Analyst* 121: 929.

### Direct Extraction

Examples of the direct approach have allowed multiple analytes, e.g. pesticides, to be determined in aqueous samples. For example, limits of detection for the determination of pesticides in water by GC with flame ionization detector (FID), nitrogen-phosphorous detector (NPD) or mass spectrometer (MS), using a 95 μm polyacrylate-coated fibre, are shown in **Table 2**. Other SPME conditions are as follows: a 50 min equilibration time with stirring at room temperature; and desorption by inserting the fibre into the hot GC injector (250°C) for 5 min. Similarly, selected detection limits for a 100 μm polydimethylsiloxane fibre are shown in **Table 3**. A typical SPME–GC–NPD chromatograph for the analysis of drinking water spiked with 36 pesticides (EPA Method 507) at the 10 μg $L^{-1}$ is shown in **Figure 6**. In addition, to evaluating the sensitivity of SPME by determining detection limits, an alternative approach is to evaluate the performance of SPME against a traditional aqueous extraction procedure (liquid–liquid extraction). Results for the extraction of 20 organochlorine pesticides extracted from a groundwater sample by both SPME and LLE are shown in **Figure 7**. In the case of SPME, a 30 μm polydimethylsiloxane fibre was inserted in a sample volume of 1.5 mL for 20 min. Desorption was achieved by insertion into the GC injector for 10 min at 260°C. The spiking level was 1 μg $L^{-1}$. For LLE a 100 mL sample spiked at the 0.5 μg $L^{-1}$ level was extracted with 20 mL, then 10 mL of hexane. The combined extracts were dried with anhydrous sodium sulfate and concentrated to 1 mL using a stream of nitrogen prior to analysis. In most cases similar results were obtained by SPME and LLE. Anomalous results for endosulfan I and II were reported.

Examples of the direct approach for non-volatile compounds, using SPME-HPLC, are shown in **Figures 8** and **9**. In Figure 8, a comparison is made between SPME and a 1 μL loop injection for the analysis of polycyclic aromatic hydrocarbons (PAHs) using reversed phase HPLC. Using the SPME-HPLC interface, as shown in Figure 2, thirteen PAHs have been analysed after sampling for 30 min using a 7 μm PDMS-coated fibre. Some differences, in terms of peak height, are noted (Figure 8) for peaks 1–4 when SPME is compared with direct injection. These differences are attributable to the selectivity of sampling associated with SPME. The versatility of the SPME-HPLC approach is further highlighted in Figure 9. In this case, an alkylphenol ethoxylate (Triton X-100) in the aqueous phase is sampled for 60 min with stirring

**Table 3** Limits of detection (ng $L^{-1}$) for selected pesticides from water using a 100 μm polydimethylsiloxane-coated fibre

| *Compound* | *NPD*[a] | *MS*[a] | *MS*[b] |
|---|---|---|---|
| Dichlorvos | 1500 | 80 | 30 |
| EPTC | 20 | 10 | 2 |
| Butylate | 50 | 20 | 1 |
| Vernolate | 100 | 20 | 1 |
| Pebulate | 40 | 10 | 14 |
| Molinate | 110 | 20 | 4 |
| Cycloate | 130 | 30 | 1 |
| Simazine | 360 | 10 | 18 |
| Atrazine | 110 | 30 | 23 |
| Propazine | 40 | 10 | 5 |
| Diazinon | 60 | 10 | 1 |
| Disulfoton | 40 | 10 | 0.7 |
| Metolachlor | 220 | 20 | 9 |

[a] Determined from 100 μg $L^{-1}$ solutions. Other SPME conditions: 20 min equilibriation time from a saturated sodium chloride solution at room temperature and pH 7. From Choudhury TK *et al.* (1996) *Environmental Science Technology* 30: 3259.
[b] Calculated for the line of best fit with a zero intercept, over the range 0.1–100 μg $L^{-1}$($n = 3$). Other SPME conditions: 50 min equilibriation time with stirring at room temperature. From Boyd-Boland AA *et al.* (1996) *Analyst* 121: 929.

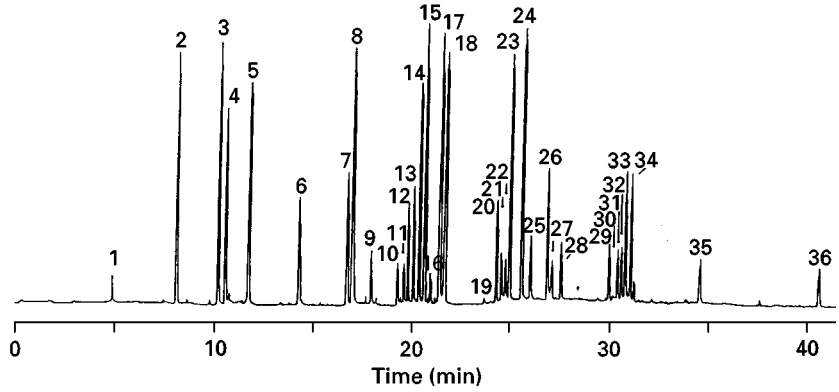


**Figure 6** SPME–GC–NPD analysis of drinking water spiked with 10 μg $L^{-1}$ each pesticide (36). (Reproduced with permission from *American Chemical Society, Environmental Science and Technology*, 30(11): 3259, 1996.) SPME conditions: 100 μm polydimethylsiloxane fibre; adsorption time, 20 min; desorption time, 5 min at 220°C. Samples were extracted with stirring at ambient temperature, at pH 7.0 and with a final 4.0 mL saturated sodium chloride solution. GC conditions: 30 m length × 0.32 mm internal diameter × 0.25 mm film 5% phenyl/95% dimethylsilicone fused silica open tubular column; temperature programme 100°C to 300°C at 4°C $min^{-1}$. 1 = dichlorvos, 2 = EPTC, 3 = butylate, 4 = vernolate, 5 = pebulate, 6 = molinate, 7 = cycloate, 8 = ethoprop, 9 = chlorpropham, 10 = simazine, 11 = atraton, 12 = prometon, 13 = atrazine, 14 = propazine, 15 = terbufos, 16 = pronamide, 17 = diazinon, 18 = disulfoton, 19 = disulfoton sulfone, 20 = simetryn, 21 = alachlor, 22 = ametryn, 23 = prometryn, 24 = terbutryn, 25 = metolachlor, 26 = triademoton, 27 = MGK 264, 28 = diphenamid, 29 = butachlor, 30 = carboxin, 31 = stirofos, 32 = fenamiphos, 33 = napropamide, 34 = merphos, 35 = norflurazon and 36 = fenarimol.

and at room temperature. Desorption is achieved by exposing the fibre for 1 min to the mobile phase. Separation is achieved using normal phase HPLC.

### Headspace SPME from Water

In headspace SPME, the fibre is exposed to the air above an aqueous sample, which is in equilibrium with

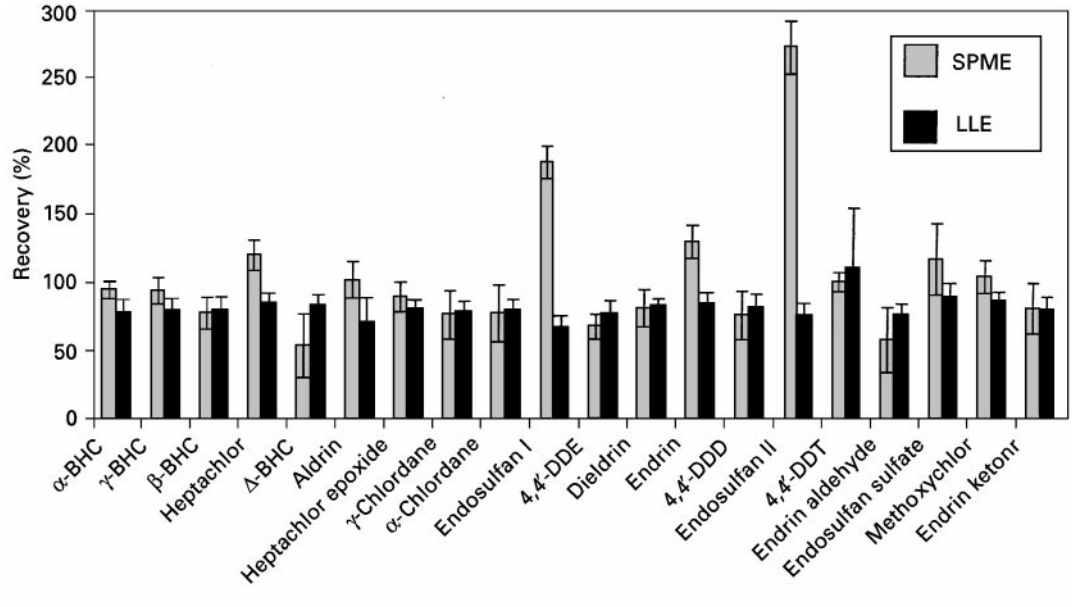


**Figure 7** Extraction of 20 organochlorine pesticides from groundwater: Comparison between SPME and LLE. (Adapted from *Journal of High Resolution Chromatography* 19: 247, 1996.) SPME conditions: 30 μm polydimethylsiloxane fibre; adsorption time, 20 min; desorption time, 10 min at 260°C. Spiking level was 1 g $L^{-1}$. Sample volume was 1.5 mL. There were three determinations. GC conditions: 30 m length × 0.25 mm internal diameter × 0.25 mm film SPB-608 fused silica open tubular column; temperature programme 100°C (4 min hold) to 150°C at 30°C $min^{-1}$ then to 300°C (8.6 min hold) at 8°C $min^{-1}$. LLE conditions: 100 mL sample extracted with 20 mL, then 10 mL hexane. Extracts were then combined, dried with anhydrous sodium sulfate and concentrated to 1 mL under a stream of nitrogen. Spiking level was 0.5 g $L^{-1}$. There were three determinations. GC conditions: 15 m length × 0.53 mm internal diameter × 0.88 mm film HP-5 fused silica open tubular column; temperature programme 150°C (0.5 min hold) to 275°C (5 min hold) at 5°C $min^{-1}$.

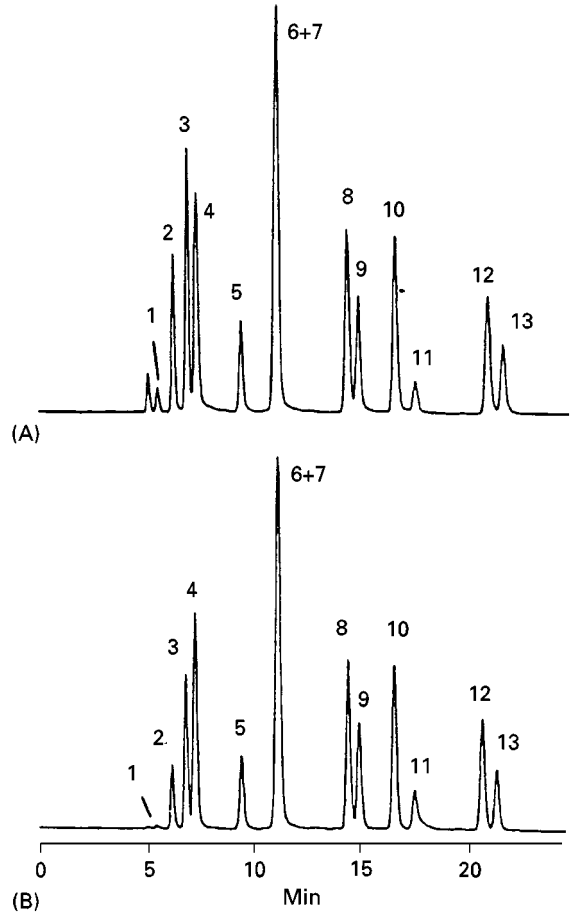


**Figure 8** Separation of polycyclic aromatic hydrocarbons by (A) 1 μL loop injection, and (B) SPME using a 7 μm PDMS-coated fibre for 30 min from 100 ppb of each compound spiked into water. (*American Chemical Society, Analytical Chemistry*, 67: 2530, 1995.) HPLC conditions: column, 25 cm × 2.1 mm internal diameter, 5 μm ODS; flow rate, 0.2 mL $min^{-1}$; (detection, UV 254 nm; solvent programme, acetonitrile–water (80 : 20, v/v) linear gradient to 100% acetonitrile in 15 min. SPME conditions: 7 μm polydimethylsiloxane fibre; adsorption time, 30 min with stirring. Spiking level was 100 ppb. Peak identification: 1 = acenaphthylene, 2 = fluorene, 3 = phenanthrene, 4 = anthracene, 5 = pyrene, 6 = benz[a]anthracene, 7 = chrysene, 8 = benzo[*b*]-fluoranthene, 9 = benzo[*k*]fluoranthene, 10 = benzo[*a*]pyrene, 11 = dibenzo[*ah*]anthracene, 12 = indeno[1,2,3-*cd*]pyrene, and 13 = benzo[*ghi*]perylene.

the aqueous phase. For this approach to be useful the analytes of interest must partition favourably into the vapour phase. Therefore, the approach is useful for volatile organic compounds in aqueous samples. Most work has been done with the BTEX compounds, i.e. benzene, toluene, ethylbenzene and the xylene isomers.

Samples and standards are introduced into glass vials, e.g. 40 mL volume, with Teflon-lined septa. It is beneficial for the speed of extraction to add a (Teflon-coated) stirring bar and/or salt for 'salting-out' to improve sensitivity. Then, each vial is capped. The septum is then pierced and the SPME device inserted. The exposed coated-silica fibre is positioned approximately l cm above the surface of the aqueous sample. The entire assembly is mounted on a magnetic stirring plate. Care is required during the stirring process that the vortex generated is not so vigorous so that the aqueous sample comes into contact with the exposed fibre (a vortex of depth 1 cm is adequate). In addition, the sample vial may be heated, by placing it in a temperature controlled water bath at temperatures in the range 40–80°C. The extraction time can be varied between 5 and 50 min, as desired. After a suitable exposure time, the fibre is retracted into its holder, withdrawn from the vial and immediately inserted into the hot injector of the GC for subsequent separation and detection. The typical performance of this type of headspace SPME is summarized in **Table 4**. The results in Table 4 compare the statistical detection limits obtained by both the headspace SPME and purge and trap approaches. In both cases, the statistical detection limits were approximately an order of magnitude higher than those required for the analysis of drinking water (US EPA Method 524.2). The use of a more sensitive detector, for instance an ion trap mass spectrometer, could lower the detection limits achievable.

## Extraction of Analytes from Solid Matrices

Traditional approaches for the extraction of analytes include Soxhlet extraction (and its variants), shake flask extraction and sonication. Soxhlet extraction is frequently referred to as the benchmark technique, so it is not suprising to find that results obtained with newer extraction techniques are compared to data obtained by Soxhlet extraction. While Soxhlet is used as the method of choice for many people for extracting analytes from solid matrices, it is a time-consuming process and uses relatively large volumes of organic solvent. Alternatives have therefore been sought to produce analytical data more rapidly and that use smaller amounts of organic solvent (or none at all). In this context, alternatives that have been proposed include supercritical fluid extraction, microwave-assisted extraction and pressurized fluid extraction. However, the high capital cost of all these alternatives and in some cases the level of expertise required to operate the instruments effectively has precluded their wide acceptance. In this context, the use of SPME has been proposed. However, in order for SPME to be of any use, the analytes must be released from the solid matrix and enter either a liquid phase or the gaseous phase. Variants on these themes for SPME are now considered.

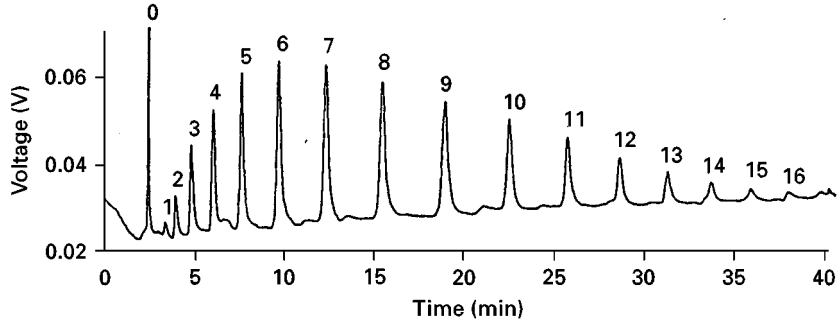


**Figure 9** Normal phase HPLC chromatogram of extracted Triton X-100. Peak assignment refers to the number of units in the ethoxylate chain. (*American Chemical Society, Analytical Chemistry* 68: 1521, 1996.) HPLC conditions: column, 25 cm × 4.6 mm internal diameter, 5 μm Supelcosil LC-$NH_2$; flow rate, 1.5 mL $min^{-1}$; detection, UV 220 nm; solvent programme, 3–53%B, where A is 90 : 10, v/v hexane–2-propanol and B is 90 : 10, v/v 2-propanol–water. SPME conditions: carbowax/template resin fibre; adsorption time, 60 min with stirring at room temperature; desorption time, 1 min. Spiking level was 100 ppm. Sample volume was 4 mL.

Several approaches can be adopted for the extraction of analytes from solid matrices using SPME. These include direct extraction of the analytes from a soil–water suspension or slurry; extraction of the analyte from the sample matrix using hot water; or, headspace extraction. In the first two approaches, it is assumed that the analytes are highly soluble in water and that water is a suitable solvent to liberate the analyte from its matrix. The latter scenario assumes that the analytes of interest are volatile or semi-volatile so that they are available in the headspace above the sample.

**Table 4** Analysis of BTEX compounds from aqueous samples: determination of statistical method detection limits (μg $L^{-1}$)[a]

| *Compound* | *Headspace SPME*[b] | *Purge and trap*[c] *EPA 524.2*[d] | |
|---|---|---|---|
| Benzene | 0.70 | 0.38 | 0.03 |
| Toluene | 0.30 | 0.37 | 0.05 |
| Ethylbenzene | 0.35 | 0.43 | 0.03 |
| m-/p-xylene | 0.23 | 0.72 | 0.05 |
| o-xylene | 0.19 | 0.30 | 0.06 |

[a]Data from MacGillivray B *et al.* (1994) *Journal of Chromatographic Sciences* 32: 317.
[b]Headspace SPME conditions: 100 μm polydimethylsiloxane fibre was used to extract BTEX compounds from a 25 mL of water containing 10.0 g of NaCl. The sample was stirred and the temperature maintained at 40°C. The extraction time was 50 min. The fibre was desorbed for 2 min at 180°C. Analysis was by GC-FID.
[c]Purge and trap conditions: 5 mL samples were purged for 10 min using a helium flow rate of 40 mL $min^{-1}$ and a sample temperature of 40°C. The compounds were trapped on a Tenax-charcoal trap. Analysis was by GC-MSD in the full scan mode.
[d]US Environmental Protection Agency guidelines for BTEX in drinking water (method 524.2). Reference: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 3.0, US EPA Office of Research and Development, Cincinnati, OH, 1989, EPA Document EPA/600/4-88/039.

### Direct (Slurry) SPME

For slurry extraction, a known quantity of sample, e.g. 10 mg to 1 g of soil, is mixed with a solvent (water) and stirred. It may be necessary to adjust the pH of the solution (to convert all compounds to a non-ionized form) and add salt to improve the extraction efficiency. The SPME fibre is then exposed directly to the resultant suspension or slurry for a prespecified time (1–60 min) and then analysed. In addition, it also assumes that the matrix itself will not interfere with the extraction process. If this is the case, the SPME fibre can be placed inside a protective membrane in the slurry. The major limitation of this approach is that the membrane itself does not preclude any of the analytes of interest. However, this approach has not yet been fully tested and further evaluation is necessary. Typical results for the analysis of chlorophenols from a contaminated land site are shown in **Table 5** using the slurry SPME approach and two methods of quantitation (direct calibration using an internal standard and the method of standard addition). The results are compared with those obtained by Soxhlet extraction. A typical SPME–GC–MS chromatogram of the soil sample is shown in **Figure 10**.

### Combined Hot Water Extraction–SPME

An alternative to the slurry method is to extract the solid sample with hot water and then isolate the analytes from the water using SPME prior to chromatographic separation and detection. This is a relatively new approach with few relevant publications to date. The basis of the approach, however, is that hot, pressurized water can selectively leach analytes from the solid matrix. Early work has suggested that the water temperature needs to be above 200°C and a pressure of 50 atm for effective

**Table 5** Slurry analysis using SPME of a soil sample: comparison with Soxhlet extraction [a]

| *Compound* | *SPME/internal standard* ($\mu g\ g^{-1}$)[b] | *SPME/standard addition* ($\mu g\ g^{-1}$)[b] | *Soxhlet extraction* ($\mu g\ g^{-1}$)[c] |
|---|---|---|---|
| 2,4-Dichlorophenol | 0.9 | 1.9 | 2.0 |
| 2,4,6-Trichlorophenol | 2.4 | 3.7 | 4.4 |
| 2,3,4,6-Tetrachlorophenol | 7.6 | 8.4 | 12.8 |
| Pentachlorophenol | 533.8 | 562.2 | 642.4 |

[a] Data from Lee MR *et al.* (1998) *Journal of Chromatography* 806: 317.
[b] SPME: 40 mg of soil in 12.5 mL of a 20 $\mu g\ L^{-1}$ internal standard (2,4,6-tribromophenol) solution and, then solution was diluted to 50 mL with pH 1 buffer solution and 5 M KCl added.
[c] Soxhlet: 2 g soil extracted with 150 mL of n-hexane–acetone (1 : 1) for 8 h. Analysis using GC-SIM-MS.

extraction of semi-volatile compounds of environmental interest including polycyclic aromatic hydrocarbons (PAHs). It is also important in this type of work to be vigilant for analyte degradation, which obviously might result in lower recoveries than expected (but also not to neglect the possibilities of formation of compounds of interest). The dynamic extraction of organic pollutants from solid matrices using water is possible using apparatus designed for supercritical fluid extraction (**Figure 11**A). By placing the soil sample in the extraction cell of the SFE apparatus, effective extraction using water can be accomplished at elevated temperature ($> 200°C$) and pressure (50 atm). Quantitation is then achieved using SPME by inserting the fibre in the water extract (Figure 11B) followed by chromatographic analysis.

Preliminary results using this type of approach are shown in **Table 6**.

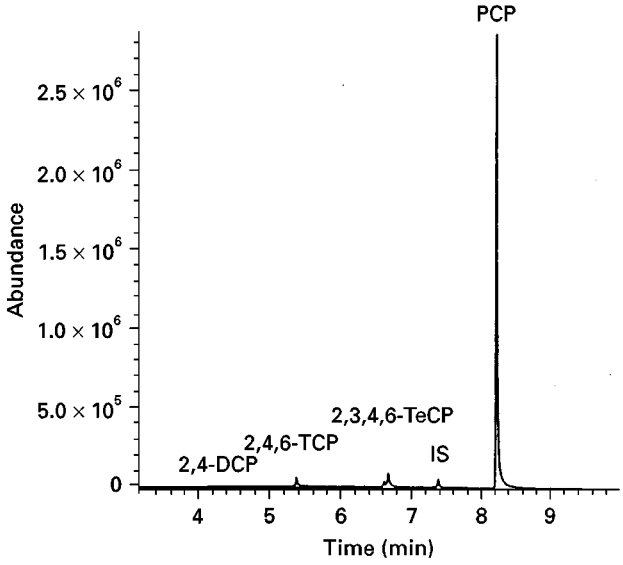


**Figure 10** SPME-GC-MS chromatogram of a real soil sample contaminated with chlorophenols. (*Journal of Chromatography A*, 806: 317, 1998, Copyright Elsevier Science.) GC conditions: column, 30 m length × 0.25 mm internal diameter × 0.5 μm film DB-5.625 fused silica; injection, splitless mode with an injector temperature of 290°C, and a splitless time of 1 min; temperature programme 60–190°C at 30°C $min^{-1}$ and from 190 to 310°C at 10°C $min^{-1}$. Slurry preparation: 40 mg of sieved soil (mesh size 1.981 mm and 2.000 mm) was prepared in 12.5 mL, of 20 $\mu g\ mL^{-1}$ internal standard solution and, then, the solution was diluted to 50 mL with pH 1 buffer solution and 5 M KCl added. SPME conditions: 85 μm polyacrylate coated fibre; adsorption time, 40 min with stirring at 1000 rpm; desorption time, 2 min at 290°C. Peak identification: 2,4-DCP = 2,4-dichlorophenol; 2,4,6-TCP = 2,4,6-trichlorophenol; 2,3,4,6-TeCP = 2,3,4,6-tetrachlorophenol;IS = 2,4,6-tribromophenol; PCP = pentachlorophenol.

## Headspace–SPME

Instead of using SPME to extract from the aqueous extract or slurried sample an alternative strategy uses headspace–SPME. In this approach SPME is used to extract volatile or semi-volatile analytes from the headspace above a solid sample. A soil sample (l0 mg to 1 g) is placed in a headspace vial and the vial is

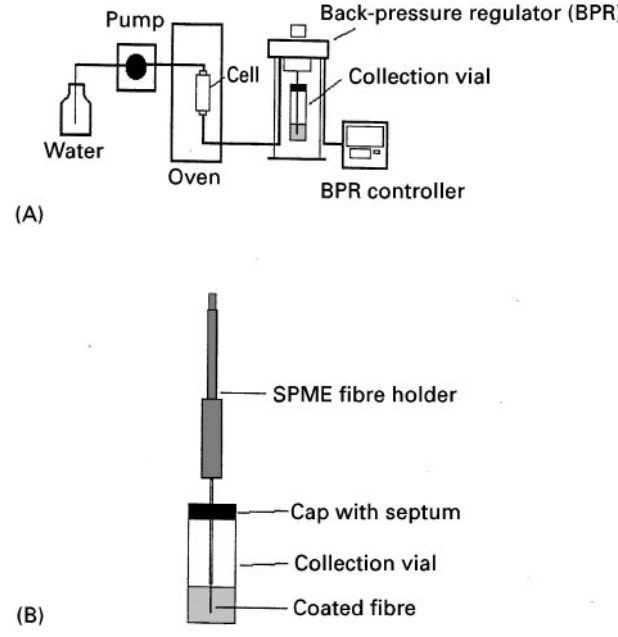


**Figure 11** Combined hot water extraction–SPME: (A) Apparatus for hot water extraction and (B) quantitation using SPME.

**Table 6** Dynamic high temperature water extraction of selected polycyclic aromatic hydrocarbons from an urban air particulate reference material (NIST 1649)[a]

| *Compound* | *Certified concentration* $\mu g\ g^{-1}$ *(%RSD)* | *Estimated concentration as % of certified concentration (%RSD) (n = 3)*[b] |
|---|---|---|
| Fluoranthene | 7.0 (7) | 134.0 (16) |
| Pyrene | 7.2 (7) | 87.5 (15) |
| Benzo[*a*]pyrene | 2.9 (17) | 72.0 (29) |

[a] Reference: Daimon H and Pawliszyn J (1996) *Analytical Communications* 33: 421.
[b] High temperature water extraction: 250°C and 50 atm.

sealed by crimping with an appropriate cap, e.g. an open-centred aluminium cap containing a PTFE/grey-butyl moulded septum. In order to promote the release of volatiles a small quantity of water (10–30%) may be added to the soil sample. In addition, the volatility of an analyte can be increased by heating the sample. This can simply be done by placing the sealed sample vial in a thermostatically-controlled water bath. It has been suggested that at ambient temperature this headspace SPME approach can be effective for three ring PAH compounds or more volatile compounds.

## Conclusion

While SPME has been applied to a wide range of application areas, it is those with an environmental theme that have been mainly used to date. The main focus of this article is on the method of operation for a range of sample types. Specific examples have been provided as to the application of SPME for extraction of analytes from aqueous and solid matrices. In addition, the different forms of analysis from aqueous samples are considered, i.e. direct and headspace sampling while for solid samples, the use of a slurry technique, prior to hot water extraction and headspace SPME is considered. The experimental data provided should act only as a guide to the potential and diverse applications of SPME.

*See also:* **II/Chromatography: Gas:** Headspace Gas Chromatography. **III/Environmental Applications:** Soxhlet Extraction.

## Further Reading

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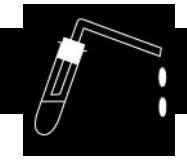
Kolb B and Ettre LS (1997) *Static Headspace-Gas Chromatography. Theory and Practice*. New York: Wiley-Interscience.
Pawliszyn J (1997) *Solid-Phase Microextraction. Theory and Practice*. New York: John Wiley.
Pawliszyn J (ed.) (1999) *Applications of Solid-Phase Microextraction*. Cambridge: Royal Society of Chemistry.

# SOLVENTS: DISTILLATION



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## Introduction

In modern chemical analysis various physicochemical methods are used to achieve high detection sensitivity. In trace analysis, reported detection levels are often measured in $\mu g\ mL^{-1}$ (ppm) $ng\ mL^{-1}$ (ppb), as well as in $pg\ mL^{-1}$ (ppt). Achievement of such low detection levels has been made possible by the use of modern analytical instruments equipped with new types of detectors and by improved sample preparation methods. Both factors are closely related to the purity of the solvents used as the mobile phases in different variants of liquid chromatography (LC), capillary zone electrophoresis (CZE), liquid–liquid (LLE) and solid-phase (SPE) extraction, filtration and flotation. Moreover, high-purity solvents are also employed to dilute samples investigated using chromatography, spectral and electrochemical analysis. Thus, solvents used in chemical analysis must fulfil many physicochemical requirements.

High-purity solvents, for example for liquid chromatography (LC) and/or for spectroscopy, are produced by many manufacturers. However, purification and quality testing of solvents are often necessary before use, particularly in the above-mentioned techniques